Controlled reactivity of terminal cyaphide complexes: Isola-tion of the 5-coordinate [Ru(dppe)2(CP)]+

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Controlled Reactivity of Terminal Cyaphide Complexes: Isolation of the 5-coordinate $[Ru(dppe)_2(C{\equiv}P)]^+$.

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Supporting Information Placeholder

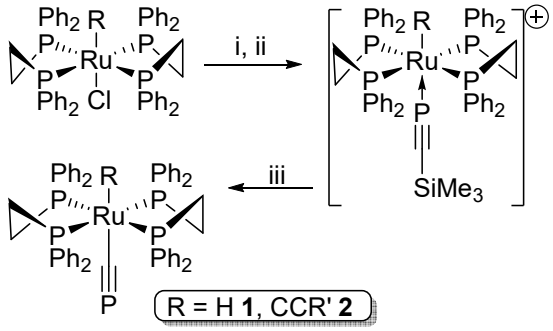
ABSTRACT: The novel cyaphide complex *trans*-$[Ru(dppe)_2Me(C{\equiv}P)]$ is obtained in excellent yields and exhibits the first instance of controlled reactivity of any terminal-cyaphide complex. Its treatment with ZnX_2 / PPh_3 effects selective metathesis of the methyl moiety to afford the unprecedented halo-cyaphide complexes *trans*-$[Ru(dppe)_2(X)(C{\equiv}P)]$ (X = Cl, Br, I), which are structurally characterized (X = Cl, Br). Exemplified with the *trans*-bromide, these compounds are susceptible to substitution of the halides by nucleophilic reagents – illustrated with Me_2Mg – and also readily undergo halide abstraction by TlOTf to afford the first hypocoordinate cyaphide complex, *viz.* $[Ru(dppe)_2(C{\equiv}P)].OTf$, which is isolable in bulk and exhibits good stability. NMR spectroscopic and crystallographic data reveal the latter to adopt a square pyramidal geometry with an accessible coordinate vacancy, which is susceptible to the addition of nucleophiles. This is illustrated analytically by reactions with Me_2Mg and $LiC{\equiv}CPh$, and with its facile bulk carbonylation to afford *trans*-$[Ru(dppe)_2(CO)(C{\equiv}P)]^+$. .

INTRODUCTION

Cyaphide ('-C≡P'), a notional analogue of cyanide or acetylide, is the very simplest, yet has been among the most elusive of the phosphacarbons. Despite the relatively extensive study of phosphaakynes (RC≡P) over the past five decades[1,2] the discrete cyaphide anion remains unknown, due to an apparently intrinsic instability,[3] while its engagement as a ligand for transition metals dates only from 1992, with Angelici's report of the transient *trans*-$Pt(PEt_3)_2Cl(C{\equiv}P)$,[4a] trapped as the η^1,η^2-*C,P*-bridged $[(Et_3P)_2Pt(Cl)(\mu{:}\eta^1{:}\eta^2\text{-}C{\equiv}P)Pt(PEt_3)_2]$.[4] The discrete *C*-terminal coordination of cyaphide was finally unequivocally demonstrated only in 2006, with Grützmacher's seminal report of $[RuH(dppe)_2(C{\equiv}P)]$ (**1**),[5] the first such complex to be isolated and structurally characterized. Subsequent activity was initially slow to develop and sparse, being limited to Russell's *in situ* observation of $[Mo(dppe)_2(\eta^1\text{-}P{\equiv}CSiMe_3)(C{\equiv}P)]^-$.[6] More recently, however, we have developed a range of complexes comprising *trans*-disposed cyaphide and alkynyl ligands that exhibit through-conjugation, *viz.* $[Ru(dppe)_2(C{\equiv}CR)(C{\equiv}P)]$ (**2**, R = CO_2Me **a**; C_6H_4R', R' = Me **b**, H **c**, F **d**, CO_2Me **e**, OMe **f**, NO_2 **g**, $C{\equiv}CRu(dppe)_2(C{\equiv}P)$ **h**),[7a-c] accessed via a modification of the Grützmacher methodology (Scheme 1). Meanwhile, Meyer has reported a single uranium species obtained via the unexpected fragmentation of the phosphaethynolate ion (^-OCP).[8]

Despite these advances the reactivity of cyaphide complexes remains an unknown, most examples either appearing inert, or exhibiting a propensity for decomposition with loss of the terminal cyaphide ligand.[5,7a] This has necessarily precluded the post-synthetic modification of such complexes, requiring that the cyaphide ligand is installed as a final synthetic step. Scope has thus been essentially limited to the availability of precursors of the type *trans*-$[Ru(dppe)_2R]^+$ and a reliance on these then being amenable to installation of an η^1-$P{\equiv}CSiR_3$ ligand; this cannot be assured, given the low basicity of phosphaalkyne lone pairs.[2] Indeed, the reluctance of this step bears significant responsibility for the dearth of such compounds reported to date.

Scheme 1. General synthetic route to precedent cyaphide complexes.[5-7]



Reagents conditions: i) MOTf (M = Ag, Tl) or $AgPF_6$, CH_2Cl_2; ii) $P{\equiv}CSiMe_3$ (in toluene); iii) NaOPh or KO^tBu, THF.

In seeking to develop and exploit the coordination and organometallic chemistry of cyaphide, it is thus essential to establish access to complexes of this ligand that are amenable to post-synthetic ligand exchange, while leaving the terminal 'C≡P' moiety intact. Herein, we report the first such examples, achieved by controlled exchange of the *trans*-ligand within a *trans*-$[Ru(dppe)_2R(C{\equiv}P)]$ scaffold, and leading ultimately to the isolation of an unprecedented 5-coordinate cyaphide-containing cation. We further illustrate the convenience

of this complex as a synthetic precursor through ligand addition at the vacant site.

RESULTS AND DISCUSSION

The ruthenium-methyl fragment $[Ru(dppe)_2Me]^+$, prepared by methide abstraction from $[Ru(dppe)_2Me_2]$, itself obtained via modification of literature protocols,[9] reacts with $P{\equiv}CSiMe_3$ to afford *trans*-$[Ru(dppe)_2(Me)(\eta^1\text{-}P{\equiv}CSiMe_3)]^+$ (**3**$^+$), subsequent treatment with stoichiometric NaOPh effecting its conversion to *trans*-$[Ru(dppe)_2(Me)(C{\equiv}P)]$ (**4**). Characteristic spectroscopic signatures for the phosphacarbon and dppe moieties confirm the formation of **3**$^+$ (δ_P 121.3, 46.7 $^2J_{PP}$ 28 Hz) and **4** (δ_P 177.9, 58.9 $^3J_{PP}$ 4 Hz), with retention of the Ru-Me fragment in each case apparent from the ^{1}H and $^{13}C\{^1H\}$-NMR spectra (δ_H –0.34, δ_C 2.7 **3**$^+$; δ_H –2.31, δ_C –9.8 **4**). The conversion of **3**$^+$ to **4** is accompanied by loss of signals associated with the silyl and triflate moieties and a significant decrease in the C≡P stretching frequency (ν_{CP} = 1217 cm^{-1} **4**, vs 1269 cm^{-1} **3**$^+$), as we have previously noted,[7] with the identity of **4** ultimately confirmed from crystallographic data (Figure 1). While the connectivity is unequivocal, disorder about the cyaphidic carbon center precludes meaningful discussion of the C≡P distance, which consequently appears truncated with respect to prior examples,[5,7] while the Ru–C_{CP} linkage is notably longer, albeit still within the range seen for Ru–C_{CC} systems recorded in the CCDC.[10] The *trans* methyl ligand and remaining core geometry are similarly comparable to respective precedents.

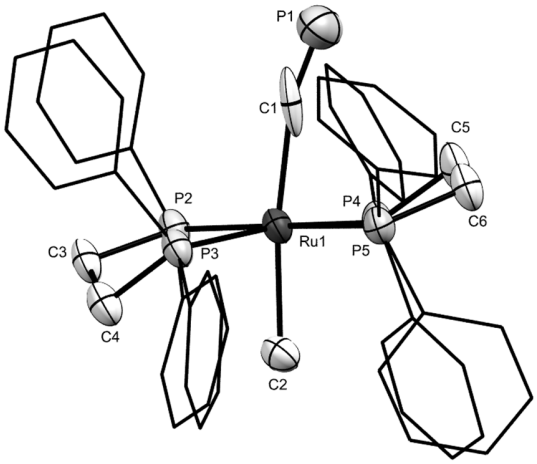
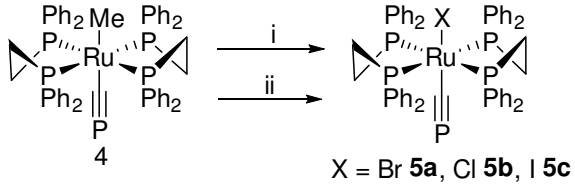


Figure 1: Molecular structure of **4** (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). C1 is disordered across two sites (90%/10%), but not readily modelled, distorting the C≡P distance. Selected bond lengths [Å] and angles [°]: P1–C1 1.392(8), Ru1–C1 2.186(8), Ru1–C2 2.238(6), Ru1–P2 2.370(2), Ru1–P3 2.364(2), Ru1–P4 2.341(2), Ru1–P5 2.338(2); P1–C1–Ru1 165.5(5), C1–Ru1–C2 171.2(3), C1–Ru1–P2 98.4(2), C1–Ru1–P3 102.13(15), C1–Ru1–P4 85.94(15), C1–Ru1–P5 82.8(2).

In seeking to coordinatively engage the cyaphide moiety of **4** its interaction with $ZnBr_2(PPh_3)_2$ was explored, resulting in the exclusive formation of a new complex (**5a**, Scheme 2). Unexpectedly, **5a** retains the characteristic spectroscopic signature of a terminal cyaphide (δ_P 135), albeit shifted to lower frequency, but with no evidence for further coordination. It is, however, devoid of signals associated with the σ-methyl ligand, the exchange of methyl for bromide being ultimately confirmed by crystallographic data (Figure 2 and SI (**5b**, *vide infra*)). These clearly illustrate the *trans*-arrangement of halide and C≡P (which are both refined equally across two sites), the C≡P distances being in line with both **1**[5a] and the alkynyl systems **2a,c-e**[7a,c] and exhibiting near perfect linear coordination, as observed in **1**, **2c** and **2d**. In contrast, the Ru–C_{CP} distances appear appreciably truncated, while the Ru–X linkages lie toward the upper bounds recoded in the CCDC (X = Cl 2.30 –2.60 Å; Br 2.45 – 2.75 Å).[10]

Scheme 2. Syntheses for 5a – c.



Reagents conditions: i) $ZnX_2(PPh_3)_2$, THF, 18 h.; ii) ZnX_2, PPh_3 (5 mol%), THF, 18 h.

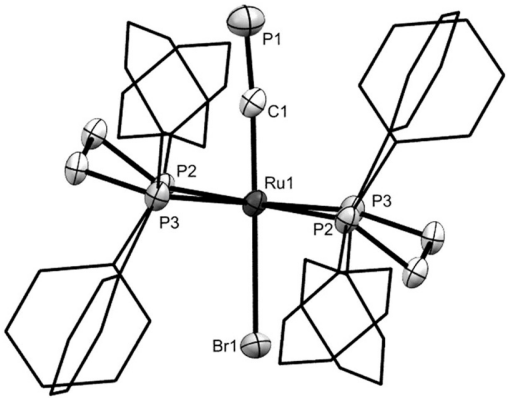


Figure 2: Molecular structure of **5a** (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). The bromide and cyaphide ligands are refined across two equal positions (50 % occupancy) such that the ruthenium atom sits on an inversion center; equivalent atoms are generated by symmetry transformation. The structure for **5b** is similar and depicted in SI. Selected bond lengths [Å] and angles [°] for **5a**: P1–C1 1.544(10), Ru1–C1 1.901(9), Ru1–Br1 2.690(2); P1–C1–Ru1 175.8(5), C1–Ru1–Br1 177.1(2), C1–Ru1–P2 97.0(2), C1–Ru1–P3 95.2(2), C1–Ru1–P2' 83.0(2), C1–Ru1–P3' 84.8(2).

Optimal formation of **5a** is achieved by replacing the zinc complex with $ZnBr_2$ and sub-stoichiometric PPh_3 (5 mol%), the analogous reactions with ZnX_2 (X = Cl, I, Scheme 2) affording respectively **5b** and **5c**, albeit that these are less amenable to bulk isolation in analytical purity. This appears, to the best of our knowledge, to be the first example of zinc-halide mediated halogen/methyl exchange at a transition metal,[11] and apparently requires the presence of at least catalytic

PPh_3, implying that $ZnX_2(PPh_3)_2$, formed *in situ*, is the active species. While we have not probed the mechanism of this conversion in detail, we can reasonably dismiss adventitious water giving rise to HX *in situ*. This follows in part from stochiometric considerations, given both the scrupulous drying of reagents and stringent observation of anaerobic conditions; moreover, we observe that the addition of stoichiometric HCl to **4** is uncontrolled, yielding only small amounts of **5b** alongside numerous unidentified species, while excess of HCl also cleaves the cyaphide moiety, giving $Ru(dppe)_2Cl_2$ as the sole identifiable product. We have also observed the reaction of **4** with $ZnBr_2$ / PPh_3 by NMR, the characteristic Ru–Me resonance of **4** (δ_H –2.3, *qnt,* J_{PH} 5.6 Hz) being replaced by a broadened ($w_{1/2}$ = 8 Hz) signal to higher frequency (δ_H –0.83). Though we have not definitively identified the species responsible, it does lie in a region consistent with Zn-Me derivatives,[12,13] which might suggest Me/X metathesis. Significantly, we observe no evidence for the liberation of CH_4,[14] discounting protonation of the methyl, and thus involvement of adventitious acid.

The formation of **5a-c** is notable, given that they have proven inaccessible by more 'traditional' routes, the trigonal pyramidal $[Ru(dppe)_2Cl]^+$ being apparently inert toward $P{\equiv}CSiMe_3$. Indeed, only by generating the cation *in situ* in the presence of a large excess of $P{\equiv}CSiMe_3$ (enabling trapping prior to relaxation to a trigonal bipyramidal geometry), could a species consistent with $[Ru(dppe)_2Cl(P{\equiv}CSiMe_3)]^+$ be observed, and then only at trace levels.[15] This has previously impeded access to this synthetically versatile series of compounds, which present obvious targets for further metathesis. Indeed, this is illustrated by treating THF solutions of **5a** with Me_2Mg, which affords some evidence for the slow regeneration of **4**. In contrast, reaction with LiC≡CPh requires the presence of TlOTf, presumably to facilitate abstraction of the halide. The latter may suggest the intermediacy of a discrete 5-coordinate species, and thus at least transient stability for the cyaphide ligand within a less encumbered coordination sphere. This possibility was probed by treating a dichloromethane solution of **5a** with stoichiometric thallium triflate, resulting in an immediate color change from yellow to deep purple, with concomitant deposition of a white precipitate. Filtration and removal of the volatiles afforded **6.OTf**, its formulation as $[Ru(dppe)_2(C{\equiv}P)]$.OTf, being ultimately confirmed crystallographically (*vide infra*).

Spectroscopically, the cyaphidic (δ_P 154; *q*, J_{PP} 7 Hz) and supporting dppe (δ_P 52.1; *d*, J_{PP} 7 Hz) resonances of $\mathbf{6}^+$ are clearly observed, their respective multiplicities implying a square-pyramidal geometry. The triflate counterion is confirmed by ^{19}F-NMR data and appears uncoordinated, which was further supported by using $AgPF_6$ in place of TlOTf, resulting in directly comparable data for the cation. We note that while one might envisage accessing $\mathbf{6}^+$ more directly by treating the *trans*-methyl complex **4** with Brookhart's acid, $[H(OEt_2)][BAr^f_4]$, this reaction is unsuccessful, leading instead to decomposition, albeit ultimately with complete demethylation and the apparent formation of trace levels of methane. While the bulk phosphorus-containing products of this reaction have not been identified, they appear devoid of cyaphide. We have also attempted to abstract methide from **4** with TlOTf (*cf.* formation of $[Ru(dppe)_2Cl]^+$), and of hydride from samples of **1** using Ph_3CBF_4; in neither instance did a reaction occur.

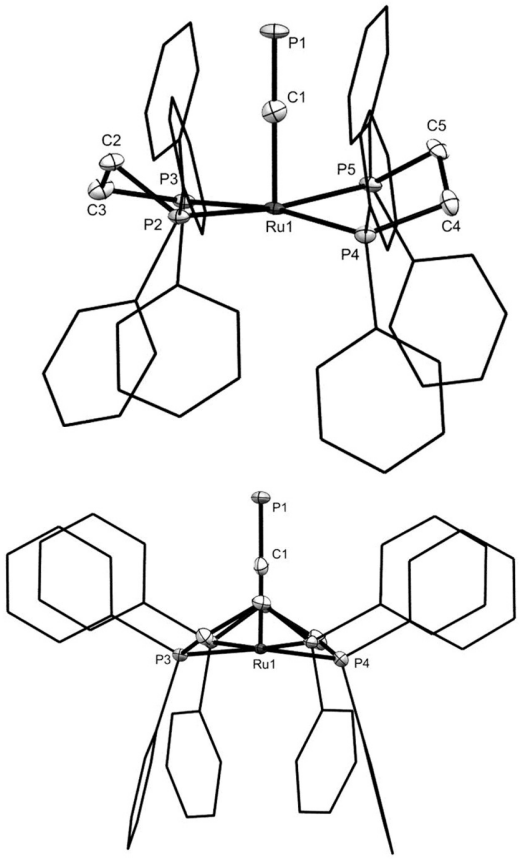


Figure 3: Orthogonal projections of the molecular structure of $\mathbf{6}^+$ in crystals of the triflate salt (ellipsoids set at 50 %, hydrogen atoms and triflate counter ion omitted and supporting ligands simplified for clarity). Within the lower projection (illustrating π-stacking between the dppe ligands) C2/C5 appear superimposed onto the Ru1–C1 bond. Selected bond lengths [Å] and angles [°]: P1–C1 1.573(4), C1–Ru1 1.904(4), Ru1–P2 2.363(1), Ru1–P3 2.380(1), Ru1–P4 2.379(1), Ru1–P5 2.351(1); P1–C1–Ru1 178.9(2), P2–Ru1–P3 81.31(3), P2–Ru1–P4 99.16(4), P3–Ru1–P5 99.91(4), P4–Ru1–P5 80.86(3), C1–Ru1–P2 86.48(13), C1–Ru1–P3 94.26(12), C1–Ru1–P4 94.88(12), C1–Ru1–P5 85.84(13).

The crystallographic data for $\mathbf{6}^+$ (Figure 3) confirm the discrete square-pyramidal complex cation, which exhibits a flattened basal plane, from which the mutually *trans* phosphines are displaced by +/- 5.5 °; this is consistent with precedent square-pyramidal ruthenium complexes bearing similarly bulky ancillary ligand sets, as recorded in the CCDC.[10] It is, however, notable that there are no direct comparators incorporating either ethynyl or cyanide ligands in the apical site, whether at ruthenium or any other group 8 or 9 metal. Indeed, though the intermediacy of 5-coordinate ruthenium alkynyl complexes is invoked[16] in the synthesis of bis(alkynyl)[17] – and, indeed, cyaphide-alkynyl[7] – complexes, relatively few discrete examples are known, while in those that are the alkynyl[18] (or cyano[19]) ligand adopts a basal, rather than apical, coordination site.

The most closely related comparator to $\mathbf{6}^+$ is thus Grützmacher's archetypal **1**, the hydride ligand of which im-

parts minimal steric perturbation. It is, however, notable that while the C≡P linkages of **1** and **6**$^+$ are near identical, the cyaphide ligand is significantly more tightly held in the cation (Ru–C 1.904(4) Å, *vs* 2.057(2) Å in **1**), presumably in part due to loss of the hydridic *trans* influence; indeed, a comparable scenario is apparent in bromide **5a** (Ru–C 1.901(9) Å), while our previously reported alkynyl derivatives (**2a,d-f**) are more in line with **1**. The geometries of **1** and **6**$^+$ are otherwise largely comparable, with **6**$^+$ exhibiting only marginal widening of the cleft formed by the flanking dppe scaffold. This appears to be a corollary of constraints imposed by π-π interactions between the dppe ligands, facilitated by the reduced sterics providing more flexibility in the coordination environment. Such minimal geometric perturbation leaves the vacant *trans* coordination site readily accessible, as illustrated by reactions with Me_2Mg and LiC≡CPh, which respectively generate **4** and **2c**.[7c]

These reactions hint at the synthetic potential of **6**$^+$, which should offer an unrivalled starting point from which to access a range of cyaphide complexes, including hitherto inaccessible variants. Indeed, a case in point is the installation of a *trans* carbonyl ligand, which we have long sought (to aid investigation of the electronic character of cyaphide) without success. Bubbling of CO through a dichloromethane solution of **6.OTf**, effects a near instantaneous color change (from purple to yellow), the subsequent removal of the volatiles yielding exclusively **7.OTf**, formulated as $[Ru(dppe)_2(CO)(C{\equiv}P)]$.OTf, on the basis of spectroscopic and crystallographic data (Figure 4).

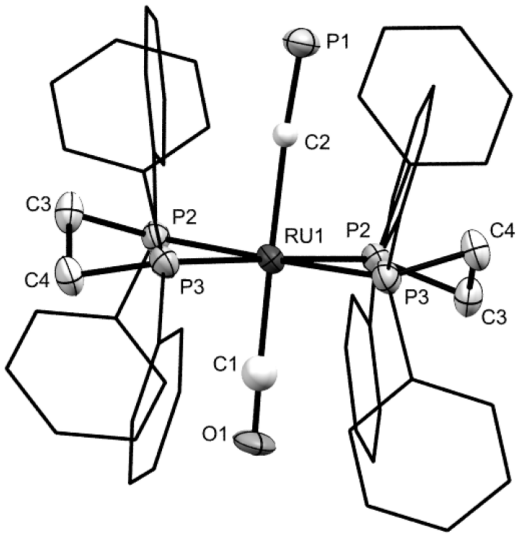


Figure 4: Molecular structure of **7**$^+$ in crystals of the triflate salt (ellipsoids set at 50 %, hydrogen atoms omitted and supporting ligands simplified for clarity). The asymmetric unit comprises two half-cations with the C≡O and C≡P ligands modelled across two positions (50 %) occupancy, this disorder requires that the respective carbon atoms be modelled isotropically.[20] The second molecule is depicted in the SI file. Selected bond lengths [Å] and angles [°]: *molecule 1 (shown)*: P1–C2 1.53(2), Ru1–C2 2.06(2), Ru1–C1 1.888(19), C1–O1 1.14(2), Ru1–P2 2.417(1), Ru1–P3 2.418(1), P1–C2–Ru1 176.0(13), C2–Ru1–C1 178.3(7), Ru1–C1–O1 177.8(17). *molecule 2 (SI)*: P≡C 1.53(2), Ru–C_{CP} 2.141(11), Ru–C_{CO} 1.815(11), C≡O 1.216(16), Ru–P5 2.399(1), Ru–P6 2.383(2), P–C–Ru 173.6(7), C_{CP}–Ru1–C_{CO} 170.0(5), Ru–C–O 175.6(10).

NMR spectroscopic data demonstrate retention of the cyaphide (δ_P 181, *q*, J_{PP} 10 Hz) and supporting dppe ligands (δ_P 43.6, *d*, *J* 10 Hz), while both cyaphide (ν_{CP} 1261 cm^{-1}) and carbonyl (ν_{CO} 1980 cm^{-1}) are apparent in the infrared spectrum. The latter is comparable to those reported for the very limited range of *trans*-$[Ru(dppe)_2(CO)(C{\equiv}CR)]$ (ν_{CO} 1977 – 1984 cm^{-1})[21] and in line with more general examples of ruthenium(II) alkynyl carbonyl complexes, with electronically similar ancillary scaffolds,[22] consistent with an alkynyl-like character for the C≡P moiety. The C≡P stretching frequency is among the highest recorded for cyaphide complexes, reflecting its *trans*-disposition from a more potent π-acid. The structural data are less conclusive due to uncertainty imparted by disorder of the C≡P and C≡O units, which also differ between two independent molecules within the cell; however, they would in general appear to reflect a truncated C≡P moiety and relatively long Ru–C_{CP} distance,[23] with the opposing trend for the C≡O ligand. Taken together, these data indicate the previously noted acceptor character of the 'C≡P' ligand,[7] though appreciable in respect of alkynyls, is weak in comparison to that of C≡O. This firmly supports assignment of the C≡P ligand as an alkynyl analogue, but with a moderately enhanced acceptor character.

CONCLUSIONS

We have described the first examples of controlled reactivity within the coordination sphere of a transition metal cyaphide complex, resulting in facile exchange of the trans ligand, while retaining the cyaphide moiety. This has afforded access – *via* an apparently novel zinc-induced demethylation – to a range of *trans*-halo cyaphides that are susceptible to further metathesis and halide abstraction, the latter affording a discrete 5-coordinate complex cation, *viz.* $[Ru(dppe)_2(C{\equiv}P)]^+$ (**6**$^+$). Isolable in bulk as the triflate salt, the latter is the first complex to feature terminally ligated cyaphide within a flexible coordination sphere, albeit that a square-pyramidal geometry is adopted, thus the C≡P moiety is only marginally less screened than in precedent examples. The geometry is apparently enforced by ligand-ligand interactions and results in a readily accessible coordinate vacancy, which is susceptible to the addition of nucleophiles. This is illustrated by treatment with Me_2Mg, which regenerates the parent complex $[Ru(dppe)_2Me(C{\equiv}P)]$ (**4**), while the reaction with LiCCPh offers access to a previously reported alkynyl derivative (**2c**).[7c] More significantly, treatment with CO affords facile access to the previously elusive $[Ru(dppe)_2(CO)(C{\equiv}P)]$OTf (**7.OTf**), data for which concur with the assignment of cyaphide as an alkynyl analogue.

The facility of ligand addition to **6**$^+$ renders it a convenient starting point from which to further develop the range of cyaphide complexes, circumventing difficulties associated with installing the C≡P ligand to a pre-formed scaffold. This both increases the accessibility of cyaphide complexes, allowing more extensive exploitation of this rare ligand, and offers potential for variation of the supporting ligands, the breadth and scope of which we are currently exploring.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or dinitrogen. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å, for CH_2Cl_2, $CHCl_3$, Et_2O, THF) or potassium mirrors. Reagents were obtained from Sigma-Aldrich, Fisher or Fluorochem and purified by appropriate methods before use; Anhydrous ZnX_2 were further purified and extended heating at >200 °C under high vacuum (10^{-7} mbar) and subliming (>250 °C, 10^{-7} mbar). Me_2Mg,[24] $Me_3SiC{\equiv}P$,[7,25] [Ru(dppe)$_2$Cl]OTf[26] and NaOPh[27] were prepared by literature methods. Unless otherwise stated NMR spectra were recorded at 303 K on a Varian VNMRS 400 (^{1}H 399.50 MHz, ^{13}C 100.46 MHz, ^{19}F 375.87 MHz, ^{31}P 161.71 MHz, ^{29}Si 79.37 MHz) spectrometer. All spectra are referenced to external Me_4Si, 85 % H_3PO_4 and $CFCl_3$ as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra, while silicon shifts were determined indirectly (HMBC). IR spectra were recorded on a Perkin Elmer Spectrum One instrument. Mass spectra were recorded by Dr A. Abdul-Sada of the departmental service and elemental analyses were obtained either by Mr S. Boyer, London Metropolitan University Analytical Service (**3.OTf**), or Pascher Labs, Germany. *CAUTION! Thallium(I) salts have acute toxicity through ingestion and inhalation, with potential long-term health impact. Ensure proper containment and PPE are used when handling these materials and all residues are collected, labelled and disposed of as containing thallium.*

X-ray diffraction studies. Single crystal X-ray diffraction data were recorded on an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector using Cu-Kα (λ = 1.54184 Å) radiation. Structure solution and refinement were performed using SHELXT[28] and SHELXL[29] respectively, running under Olex-2.[30]

Synthesis of [Ru(dppe)$_2$Me$_2$]. In a modification of the procedure for [Ru(dppm)$_2$Me$_2$],[9] a mixture of [RuCl(dppe)$_2$]OTf (2.260 g, 2.09 mmol) and Me_2Mg (0.185 g, 3.41 mmol) was suspended in Et_2O (*ca* 50 cm^3) at ambient temperature, resulting in an immediate colour change from red to yellow-brown; the resulting solution was stirred for 18 hours. Filtration afforded a yellow/brown solid, which was washed with Et_2O (3 x 20 cm^3) and dried *in vacuo*. The compound was confirmed by reference to related literature data,[9] then used directly in the subsequent step. Yield: 2.00 g, 89 %. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=6.55–7.49 (*m (br),* dppe), 2.41 (8H, *m (br),* C_2H_4), -1.18 (6H, *qnt, J* = 4.36 Hz, CH_3). ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P- 59.2 (4H, *s,* PPh_3). The bulk has *cis/trans* ratio of ca 5:95 and is used in crude form for the next step.

Synthesis of [Ru(dppe)$_2$Me]OTf. A mixture of [Ru(dppe)$_2$Me$_2$] DCM (1.689 g, 1.57 mmol) and TlOTf (0.569 g, 1.61 mmol) was suspended in CH_2Cl_2 (30 cm^3) and allowed to stir for 1 hour, resulting in a gradual color change from yellow-brown to red-purple. The mixture was filtered via cannula and volatiles removed from the filtrate under reduced pressure, to afford a red-purple solid that was dried *in vacuo*. Compound identity was confirmed by reference to literature data.[31] Yield: 0.980 g, 59%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=7.38 (8H, *m (br),* dppe), 7.22 (8H, *t*, *J* = 7.6 Hz, dppe), 7.14 (8H, *t*, J_{HH} = 7.6 Hz, dppe), 6.78 (16H, *d*, J_{PH} = 6.5 Hz, dppe), 2.51 (8H, *m (br),* C_2H_4), -0.9 (3H, *m (br),* CH_3). ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=55.7 (4H, *s,* PPh_3). Compound is used without further purification in the next step.

Synthesis of *trans*-[Ru(dppe)$_2$Me(η^1-P≡CSiMe$_3$)]OTf (3.OTf). To a stirred suspension of [Ru(dppe)$_2$(Me)]OTf (1.36 g, 12.1 mmol) in 1,4-dioxane (*ca* 20 cm^3) was added $Me_3SiC{\equiv}P$ (25 cm^3, 0.05 mol dm^{-3}, 12.5 mmol), then the mixture left to stir for 1 hour. The resulting precipitate was isolated by filtration (cannula) and dried *in vacuo* to afford **3.OTf** as a cream solid. The bulk sample retains an equivalent of dioxane and trace levels of apparently the cis isomer. Yield: 1.068 g, 71%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=7.51 (8H, *m (br), meta*-C_6H_5), 7.5 (4H, *t*, *J* = 7.3 Hz, *para*-C_6H_5), 7.4 (4H, *t*, *J* = 7.5 Hz, *para'*-C_6H_5), 7.3 (8H, *t*, *J* = 7.3 Hz, *ortho*-C_6H_5), 7.1 (8H, *t*, *J* = 7.3 Hz, *ortho*-C_6H_5), 6.8 (8H, *m (br), meta*-C_6H_5), 2.7 (8H, *m (br),* C_2H_4), -0.01 (9H, *s*, $SiMe_3$), -0.35 (3H, *m (br),* CH_3); ^{13}C{^{1}H}-NMR (100.45 MHz, CD_2Cl_2): δ_C=184.8 (*d*, *J* = 69 Hz, C≡P), 134.7 (*qnt, J* = 10.01 Hz, *ipso*-C_6H_5), 133.4 (*qnt, J* = 2.56 Hz, *meta*-C_6H_5), 132.8 (*qnt, J* = 2.10 Hz, *meta*-C_6H_5), 131.1 (*s, para*-C_6H_5), 130.5 (*s, para*-C_6H_5), 128.6 (*qnt, J* = 2.34 Hz, *ortho*-C_6H_5), 128.4 (*qnt, J* = 2.36 Hz, *ortho*-C_6H_5), 28.9 (*qnt, J* = 11.7 Hz, CH_2CH_2), 2.12 (*m*, CH_3), 0.35 (d, *J* = 5.11 Hz, $SiMe_3$); ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P 121.3 (1P, *qnt*, *J* = 28 Hz, C≡P), 46.7 (4P, *d, J* = 28 Hz, PPh_2); ^{19}F NMR (375.86 MHz, CD_2Cl_2): δ_F –78.9 (*s*, OTF); ^{29}Si NMR (79.37 MHz, CD_2Cl_2): δ_{Si} 15.4 (Ru-PCSiMe_3). IR (solid, ATR) ν/cm^{-1}: 1269 (C≡P). Calcd for $C_{60}H_{60}P_5F_3O_3SSiRu.C_4H_8O_2$: C; 59.57 %, H; 5.31 %. Found: C; 59.89 %, H; 5.18 %.

Synthesis of *trans*-[Ru(dppe)$_2$Me(C≡P)] (4). A solution of **3.OTf** (1.068 g, 0.91 mmol) in THF (*ca* 20 cm^3) was cooled to -30 °C, prior to drop-wise addition of a solution of NaOPh (0.138 g, 1.2 mmol) in THF (*ca* 5 cm^3) over the course of 10 minutes. Upon complete addition the mixture was stirred for ca 2 min, removed from cold bath and the volatiles immediately removed under reduced pressure to afford a yellow-brown solid, which was washed with acetonitrile (*ca* 3 x 15 cm^3) and dried *in vacuo*, yielding a yellow solid. Yield: 0.543 g, 63%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=8.4 (8H, m (br), *meta*-C_6H_5), 7.3 (4H, *t*, *J*=7.3 Hz, *para*-C_6H_5), 7.2 (8H, *t*, *J*=7.5 Hz, *ortho*-C_6H_5), 7.1 (4H, *t*, *J*=7.4 Hz, *para*-C_6H_5), 6.9 (8H, *t*, *J*=7.6 Hz, *ortho*-C_6H_5), 6.5 (8H, *d*, *J*=7.5 Hz, *meta*-C_6H_5), 2.6 (8H, *m (br),* C_2H_4), -2.3 (3H, *qnt, J*=5.6, CH_3); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C=294 (*m (br)*, C≡P),[32] 139.1 (*qnt, J_{CP}*=9.77 Hz, *ipso*-C_6H_5), 135.9 (*qnt, J_{CP}* =9.90 Hz, *ipso*-C_6H_5), 136.1 (*m(br), meta*-C_6H_5), 134.7 (*qnt, J_{CP}* = 2.02 Hz, *meta*-C_6H_5), 129.8 (*s, para*-C_6H_5), 128.5 (*s, para*-C_6H_5), 127.4 (*qnt, J_{CP}*=1.99 Hz, *ortho*-C_6H_5), 127.2 (*qnt, J_{CP}*=2.33 Hz, *ortho*-C_6H_5), 30.9 (*s*, CH_2CH_2), -10.0 (*m (br)*, CH_3); ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=177.9 (1P, *m (br)*, C≡P), 58.9 (4P, *d, J_{PP}*=4.3 Hz, PPh_2). IR (solid, ATR) ν/cm^{-1}: 1217 (C≡P), 3046 (CH_3). Anal. Calcd for $C_{54}H_{51}P_5Ru$: C; 67.85 %, H; 5.38 %. Found: C; 68.13 %, H; 5.43 %. *Crystal data for **4 (CCDC 1938745):*** Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. $C_{54}H_{51}P_5Ru$ (M_w = 955.83 g mol^{-1}), *monoclinic, P 21/c* (No. 14), *a*=23.6755(12), *b*=11.5267(6), *c*=17.2942(8) Å, β=104.670(5), *V*=4565.7(5) Å^3, *Z*=4, *T*=173(2) K, μ*(Cu-Kα)*=4.712 mm^{-1}, D_c=1.391 Mg m^{-3}, 8676 independent reflections, full matrix F^2 refinement R_1=0.0614 on 6218 independent absorption corrected reflections, [$I > 2\sigma(I)$; $2\theta_{max}$= 142.45 °], 543 parameters, wR_2= 0.1573 (all data).

Synthesis of *trans*-[Ru(dppe)$_2$Br(C≡P)] (5a). Anhydrous $ZnBr_2$ (0.305 g, 1.35 mmol), 5mol% PPh_3 (0.017 g, 0.065 mmol) and **4** (1.289 g, 1.35 mmol), were combined in a Schlenk prior to the addition of THF (*ca* 20 cm^3). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vaco*. Yield: 1.027 g, 75%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=7.6 (8H, m (br), *meta*-C_6H_5), 7.32 (4H, m (br), *meta*-C_6H_5), 7.26 (8H, d*t*, *J*=7.5, 20.0 Hz, *para*-C_6H_5), 7.10 (16H, d*t*, *J*=7.6, 21.7 Hz, *ortho*-C_6H_5), 2.9 (8H, *m (br),* C_2H_4); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C=136.7 (*m (br)*, *ipso*-C_6H_5), 136.2 (*m (br)*, *meta*-C_6H_5), 135.8 (*qnt, J_{CP}*=2.3 Hz, *meta*-C_6H_5), 130.5 (*s, para*-C_6H_5), 130.3 (*s, para*-C_6H_5), 128.1 (*m, ortho*-C_6H_5), 31.4 (*qnt, J_{CP}*=11.6 Hz, CH_2CH_2) the cyaphide carbon could not be resolved;[32] ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=135.4 (1P, *m (br)*, C≡P), 44.8 (4P, *d, J_{PP}*=4.3 Hz, PPh_2). IR (solid, ATR) ν/cm^{-1}: 1249 (C≡P). HRMS (ESI): *m/z* calcd. for $[C_{53}H_{48}P_5BrRu]^+$: 1020.0659; Found: 1020.0577 [RMS Err 8 ppm]. Anal. Calcd for $C_{53}H_{48}P_5BrRu$: C; 62.36 %, H; 4.74 %. Found: C; 61.6 %, H; 4.73 %. *Crystal data for **5 (CCDC 1938746):*** Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. $C_{53}H_{48}BrP_5Ru$ (M_w =1020.73 g mol^{-1}), *triclinic, P–1* (No. 2), *a*=10.155(1), *b*=10.5071(12), *c*=12.593(1) Å, α=71.169(9), β=85.317(7), γ=62.172(12), *V*=1120.8(2) Å^3, *Z*=1, *T*=173(2) K, μ*(Cu-Kα)*=5.844 mm^{-1}, D_c=1.512 Mg m^{-3}, 4334 independent reflections, full matrix F^2 refinement R_1=0.0340 on 3412 independent absorption corrected reflections, [$I > 2\sigma(I)$; $2\theta_{max}$= 145.78 °], 286 parameters, wR_2= 0.0747 (all data).

Synthesis of *trans*-[Ru(dppe)$_2$Cl(C≡P)] (5b). Anhydrous $ZnCl_2$ (0.007 g, 0.052 mmol), PPh_3 (0.001 g, 0.003 mmol) and **4** (0.050 g, 0.052 mmol), were combined in a Schlenk prior to the addition of THF (*ca* 5 cm^3). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vacuo*. Yield: 0.035 g, 80%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H 7.8 (8H, m (br), *meta*-C_6H_5), 7.3 (8H, m (br), *meta*-C_6H_5), 7.26 (8H, *dt*, *J*=7.4, 16.00 Hz, *para*-C_6H_5), 7.06 (16H, *dt*, *J*=7.6, 15.86 Hz, *ortho*-C_6H_5), 2.9 (8H, *m (br),* C_2H_4); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C 265.4 (*m (br)*, C≡P),[32] 136.6 (*qnt, J_{CP}*=10.3 Hz, *ipso*-C_6H_5), 135.7 (*m (br)*, *meta*-C_6H_5), 135.6 (*qnt, J_{CP}*=2.5 Hz, *meta*-C_6H_5), 135.4 (*qnt, J_{CP}*=10.4 Hz, *ipso*-C_6H_5), 130.1 (*s, para*-C_6H_5), 130.0 (*s, para*-C_6H_5), 127.4 (*dqnt, J_{CP}*=2.6, 2.31, 4.6 Hz, *ortho*-C_6H_5), 31.0 (*s*, CH_2CH_2). ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P 132 (1P, *m (br)*,[32] C≡P), 46.2 (4P, *d, J_{PP}*=4.2 Hz, PPh_2). IR (solid, ATR) ν/cm^{-1}: 1250 (C≡P). HRMS (ESI): *m/z* calcd. for $[C_{53}H_{48}P_5ClRu]^+$: 976.1169; Found: 976.1240 [RMS Err 7 ppm]. This compound routinely analyses > 10 % low on carbon; presumably reflecting a trace level of high-mass contaminant, which we have been unable to identity. *Crystal data for **5b (CCDC 1938747):*** Crystals were grown by layering of a saturated solution in dichloromethane with hexane at ambient temperature. $C_{53}H_{48}ClP_5Ru$ (M_w =976.28 g mol^{-1}), *monoclinic, P 21/c* (No. 14), *a*=23.6006(6), *b*=11.4193(3), *c*=17.2737(4) Å, β=103.781(3), *V*=4521.3(2) Å^3, *Z*=4, *T*=173(2) K, μ(*Cu-K*α)=5.303 mm^{-1}, D_c=1.434 Mg m^{-3}, 6901 independent reflections, full matrix F^2 refinement R_1=0.0438 on 5275 independent absorption corrected reflections, [$I > 2\sigma(I)$; $2\theta_{max}$= 122.32 °], 569 parameters, wR_2= 0.1123 (all data).

Synthesis of *trans*-[Ru(dppe)$_2$I(C≡P)] (5c). Anhydrous ZnI_2 (0.008 g, 0.025 mmol), PPh_3 (0.001 g, 0.003 mmol) and **4** (0.023 g, 0.024 mmol), were combined in a Schlenk prior to the addition of THF (*ca* 5 cm^3). The resulting solution was stirred for 18 hours, leading to the precipitation of a yellow solid, which was isolated by filtration (cannula) and dried *in vaco*. Yield: 0.020 g, 75%. Poor solubility has proven limiting for the acquisition of spectroscopic data, and the material has not been obtained in analytical purity. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H 7.5 (8H, m (br), C_6H_5), 7.4 (8H, m (br), C_6H_5), 7.3 (8H, *dt*, *J*=7.4, 15.5 Hz, C_6H_5), 7.1 (16H, *dt*, *J*=7.6, 15.9 Hz, C_6H_5), 2.9 (8H, *m (br),* C_2H_4); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C=137.0 (*unres., ipso*-C_6H_5), 136.0 (*br*, *meta'*-C_6H_5), 135.4 (*br, ipso'*-C_6H_5), 135.2 (*br*, *meta*-C_6H_5), 130.2 (*br, para'*-C_6H_5), 129.8 (*br, para*-C_6H_5), 127.6 (*br, ortho*-C_6H_5), 127.5 (*br, ortho'*-C_6H_5), 30.5 (unres.,CH_2CH_2) (cyaphide carbon not resolved);[32] ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P 140 (1P, *m (br)*, C≡P), 42.1 (4P, *d (br),* PPh_2). ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P 140 (1P, *m (br)*, C≡P), 42.1 (4P, *d (br),* PPh_2).

Synthesis of [Ru(dppe)$_2$(C≡P)].OTf (6.OTf). Compound **5a** (0.400 g, 0.39 mmol) was combined with TlOTf (0.140 g, 0.39 mmol) prior to the addition of CH_2Cl_2 (*ca* 20 cm^3). The resulting solution was stirred for ca. 2 hours, before separating from the TlBr by filtration (cannula). The volatiles were removed from the filtrate under reduced pressure to afford a purple solid, which was dried *in vacuo*. The sample can be further purified by recrystalization from benzene, yielding the benzene solvate. Yield: 0.365 g, 87%. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=7.7 (8H, m (br), *meta*-C_6H_5), 7.4 (4H, *t, J*=7.5 Hz, *para*-C_6H_5), 7.3 (4H, *t*, *J*=7.5 Hz, *para*-C_6H_5), 7.1 (16H, *t*, *J*=7.6 Hz, *ortho*-C_6H_5), 6.5 (8H, m (br), *meta*-C_6H_5), 3.0 (4H, *qnt, J=8*.0 Hz C_2H_4), 2.6 (4H, *qnt, J*=8.0 Hz C_2H_4); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C=265 (*m (br)*, C≡P),[32] 134.1 (*m (br)*, *meta*-C_6H_5), 133.4 (*qnt, J_{CP}*=2.9 Hz *meta*-C_6H_5), 132.3 (*m, ipso*-C_6H_5), 131.9 (*s, para*-C_6H_5), 131.2 (*s, para*-C_6H_5), 129.7 (*qnt, J_{CP}*=2.1 Hz, *ortho*-C_6H_5), 128.7 (*qnt, J_{CP}*=2.5 Hz, *ortho*-C_6H_5), 121.5 (*q*, J_{CF}=320 Hz, CF_3), 29.4 (*qnt, J_{CP}*=11.7 Hz, CH_2CH_2); ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=154 (1P, *qnt, J_{PP}*=7.2 Hz, C≡P), 52.1 (4P, *d, J_{PP}*=7.2 Hz, PPh_2); ^{19}F NMR (375.86 MHz, CD_2Cl_2): δ_F −78.9 (*s*, OTF). IR (solid, ATR) ν/cm^{-1}: 1242 (C≡P). Anal. Calcd for $C_{54}H_{48}P_5F_3O_3SRu.0.66(C_6H_6)$: C; 61.00 %, H; 4.59 %. Found: C; 61.70 %, H; 4.66 % (recrystalized sample as benzene solvate). *Crystal data for **6.OTF (CCDC 1938748):*** Crystals were obtained by slow recrystallization from benzene at ambient temperature. $C_{53}H_{48}P_5Ru,SO_2CF_2.(1.5C_6H_6)$ (M_w =1207.07 g mol^{-1}), *triclinic, P −1* (No. 2), *a*=10.8285(2), *b*=13.5818(3), *c*=19.4936(4) Å, α=99.007(2), β=102.137(2), γ=91.643(2), *V*=2762.65(10) Å^3, *Z*=2, *T*=100(2) K, μ(*Cu-K*α)=4.487 mm^{-1}, D_c=1.451 Mg m^{-3}, 10477 independent reflections, full matrix F^2 refinement R_1=0.0506 on 9214 independent absorption corrected reflections, [$I > 2\sigma(I)$; $2\theta_{max}$= 143.20 °], 685 parameters, wR_2= 0.1265 (all data).

Synthesis of [Ru(dppe)$_2$(CO)(C≡P)].OTf (7.OTf). CO gas was bubbled through a dichloromethane solution of **6.OTf** (0.094 g, 0.086 mmol) for 2 min, resulting in a color change of the solution from purple to pale yellow. Removal of the volatiles under reduced pressure afforded **7.OTf** as an off-white solid as a mono-CH_2Cl_2 solvate. ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H=7.57 (8H, m (br), *meta*-C_6H_5), 7.45 (4H, *t, J*=7.3 Hz, *para'*-C_6H_5), 7.42 (4H, *t*, *J*=7.4 Hz, *para*-C_6H_5), 7.23 (8H, *t*, *J*=7.5 Hz, *ortho'*-C_6H_5), 7.19 (8H, *t*, *J*=7.3 Hz, *ortho*-C_6H_5), 7.01 (8H, m (br), *meta'*-C_6H_5), 3.08 (4H, *qnt, J*=8 Hz C_2H_4), 2.65 (4H, *qnt, J*=8 Hz C_2H_4); ^{13}C{^{1}H} NMR (100.46 MHz, CD_2Cl_2): δ_C=249 (*m (br)*, C≡P),[32] 200.5 (*qnt,d. J_{CP}* 10 Hz, 4 Hz, C≡O), 134.8 (*qnt*, J_{CP} 2 Hz, *meta*-C_6H_5), 133.4 (*qnt, J_{CP}*=11 Hz *ipso'*-C_6H_5), 132.9 (*qnt, J_{CP}* 2.7 Hz, *meta'*-C_6H_5), 131.9 (*s, para'*-C_6H_5), 131.7 (*s, para*-C_6H_5), 131.0 (*qnt, J_{CP}*=12 Hz, *ipso*-C_6H_5), 129.5 (*qnt, J_{CP}*=2 Hz, *ortho'*-C_6H_5), (*qnt, J_{CP}*=2.5 Hz, *ortho*-C_6H_5), 121.5 (*q*, J_{CF}=322 Hz, CF_3), 30.0 (*qnt, J_{CP}*=11.7 Hz, CH_2CH_2); ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=181.3 (1P, *qnt, J_{PP}*=10 Hz, C≡P), 52.1 (4P, *d, J_{PP}*=10 Hz, PPh_2); ^{19}F NMR (375.86 MHz, CD_2Cl_2): δ_F −78.9 (*s*, OTF). IR (solid, ATR) ν/cm^{-1}: 1980 (CO), 1261 (C≡P). Anal. Calcd for $C_{55}H_{48}F_3O_3P_5SRu.(CH_2Cl_2)$: C; 55.91 %, H; 4.19 %. Found: C; 55.61 %, H; 4.08 %. *Crystal data for **7.OTF (CCDC 1947211):*** Crystals were obtained by slow recrystallization from benzene at ambient temperature. $C_{55}H_{48}F_3O_3P_5SRu.(C_6H_6)$ (M_w =1196.02 g mol^{-1}), *monoclinic, C2/c* (No. 15), *a*=23.3771(4), *b*=12.6192(3), *c*=37.6417(9) Å, β=101.416(2), *V*=10884.6(4) Å^3, *Z*=8, *T*=100(2) K, μ(*Cu-K*α)=4.564 mm^{-1}, D_c=1.460 Mg m^{-3}, 10225 independent reflections, full matrix F^2 refinement R_1=0.0546 on 8252 independent absorption corrected reflections, [$I > 2\sigma(I)$; $2\theta_{max}$= 143.40 °], 830 parameters, wR_2= 0.1257 (all data).

Treatment of 4 with HCl. To an NMR sample of **4** in CD_2Cl_2 was added 1 equivalent, or an excess, of HCl in Et_2O (1 M). The sample were sealed and repeatedly inverted (rotor) overnight then analyzed by ^{31}P{^{1}H} NMR.

Treatment of 4 with [H(OEt$_2$)$_2$][BAr$^f_4$]. To an NMR sample of **4** in CD_2Cl_2 was added 1 equiv. Brookhart's acid. The sample was sealed and agitated, then monitored by NMR after 5 min. and upon completion.

NMR scale reaction of 4 with $ZnBr_2$ / PPh_3 (*in situ*). To a solution of **4** in THF (with C_6D_6 capillary) was added 1 equiv. $ZnBr_2$ and ca 10 mol% PPh_3. The sample was sealed and agitated until completion then observed by ^{31}P{^{1}H} NMR.

Reaction of 5a with Me_2Mg. Samples of **5a** (31 mg, 0.03 mmol) and Me_2Mg (3 mg, 0.04 mmol) were combined in THF (*ca* 10 cm^3) and stirred overnight. The mixture was filtered to remove magnesium salts, then free volatiles removed under reduced pressure and the crude product analyzed by ^{1}H and ^{31}P{^{1}H} NMR in CD_2Cl_2. Key signatures for **4:** ^{1}H NMR (399.5 MHz, CD_2Cl_2): δ_H -2.1 (3H, *qnt, J*=5.6 Hz, CH_3), 2.6 (14H, *m (br),* C_2H_4, **4+** unknown). ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=179.8 (1P, *m (br)*, C≡P), 60.7 (4P, *d, J_{PP}*=4.3 Hz, PPh_2). Solvent shift effects (cf. pure **4**) result from appreciable residual THF in the solvent mixture – we have noted, but not probed, significant shift changes between CH_2Cl_2 and THF.

Reaction of 6$^+$ with LiCCPh. To a sample of **6$^+$**, generated *in situ* from **5a** (50 mg, 0.05 mmol) and TlOTf (2 mg, 0.05 mmol) in THF (5 cm^3) was added one equivalent of LiCCPh in THF (5 cm^3) and the mixture stirred overnight. The volatiles were removed and the crude material analyzed by ^{31}P{^{1}H} NMR in CD_2Cl_2, indicating >80 % conversion: **2c:** ^{31}P{^{1}H} NMR (161.71 MHz, CD_2Cl_2): δ_P=161.7 (1P, *br*, C≡P), 51.0 (4P, *d, J_{PP}*=3.6 Hz, PPh_2) (> 80 %). **6$^+$:** ^{31}P{^{1}H} NMR

(161.71 MHz, CD_2Cl_2): δ_P=154 (1P, *qnt, J_{PP}*=7.2 Hz, C≡P), 52.5 (4P, *d, J_{PP}*=7.2 Hz, PPh_2) (< 20 %).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{19}F-NMR, 2D (^{1}H-^{13}C HSQC, HMBC; ^{1}H-^{29}Si HMBC) spectra for all compounds as appropriate; high-resolution mass spectra (HRMS) for **5a** and **5b**; ORTEP plot and selected distances / angles for **5b** and second molecule of **7**$^+$ (PDF)

Accession Codes

CCDC 1938745-1938748 and 1947211 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax:+44 1223 336033

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Notes

The authors declare no competing financial interest.

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Synopsis – For table of contents only

The first example of controlled reactivity in the presence of the cyaphide ligand is achieved by zinc-mediate methyl/halide exchange within [Ru(dppe)$_2$Me(C≡P)] to afford [Ru(dppe)$_2$X(C≡P)] (X = Cl, Br, I). Halide abstraction from the bromide yields the isolable 5-coordinate cation [Ru(dppe)$_2$(C≡P)]$^+$, which reacts with nucleophile (R^-) and neutral donors (CO), giving facile access to the respective *trans*-cyaphide complexes.

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